

Polymer Surface with Increased Hydrophilicity and Method of Making

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Government License Clause

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Field of Invention

[0002] The present invention relates to the field of chemical surface treatments and, more particularly, to polymers having at least one modified surface for increased hydrophilicity and a method of making same.

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Background of the Invention

[0003] *Hydrophilicity* describes a general property of a material surface associated with high wettability and liquid or aqueous adhesion. While many polymers are light weight, strong, and have high chemical resistance, they are typically not hydrophilic and hinder formation of a continuous film or coating on a surface of the polymer. Examples of non-hydrophilic, also known as hydrophobic, polymers include polypropylene,

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polyethylene, polystyrene, and fluoro-polymers (e.g., polyvinylidenedifluoride, polytetrafluoroethylene, etc.). Accordingly, hydrophobic polymers are not ideal for use in many applications requiring a surface having a high affinity for water. For example, hydrophobic polymers have limited efficacy as a packing material in separation columns used for mass transport processes.

[0004] Packing materials cause a liquid stream to spread over a large surface area to improve mass transfer between the liquid stream and a gas phase during: (1) distillation, where compounds are separated by condensation temperature, (2) absorption, where compounds are removed from the gas phase into the liquid stream, and (3) stripping, where volatile compounds are removed from the liquid stream into the gas phase. Three basic types of packing material currently exist – metal, ceramic, and plastic. Generally, ceramic packing materials have the advantage of being highly hydrophilic and structurally, thermally, and chemically durable. However, ceramic materials are dense, heavy, and difficult to form into high surface area shapes. Additionally, the weight of ceramic packing materials requires a stronger, more expensive vessel or column and tends to crush elements near the bottom of the column. High surface area designs are more fragile and exacerbate the crushing problem. Structurally stronger and simpler shapes result in greater flow resistance, which requires larger fans or gas pumps to move gas through the column. Simpler shapes also have a lower surface area to volume ratio and require greater volumes to achieve the desired surface area.

[0005] Metal packings are structurally stronger and are more easily formed into a given shape than ceramics. However, while metal packings provide many of the same

advantages as their ceramic counterparts, they are not chemically compatible with many aqueous-based separation processes, especially those involving acidic gasses.

[0006] Polymer packing materials are advantageous because they are lightweight and easily formed into complex, three-dimensional, open or wireframe-type shapes that provide more surface area per unit mass or volume. One example of a high surface area polymer packing material is the Q-PAC product available from Lantec Products, Inc. in Agoura Hills, CA. Similar wireframe-type polymer packings are produced by Koch-Glitsch and Jager, Inc. However, because plastic is much less hydrophilic than ceramic, the aqueous phase tends to flow in rivulets rather than forming uniform films, which maximizes the available surface area. Therefore, to achieve the desired mass transfer, columns filled with conventional polymer packing materials must have relatively larger volumes resulting in increased costs.

[0007] Several methods exist to chemically treat polymer surfaces for increased hydrophilicity. However, many of these methods are not effective for the previously-mentioned hydrophobic polymers. For example, mere liquid- or gas-phase chemical reactions are not highly effective at increasing the wettability of certain highly-chemically inert polymers such as polyethylene, polypropylene, and the halogenated analogues of these basic polymers. Moreover, many methods described in the art suffer from one or more of the following disadvantages:

[0008] (1) low throwing power, which describes the ability of a particular surface treatment process to conformally affect irregularly shaped features on a surface and restricts the use of such a treatment process to polymer surfaces having relatively simple geometries and a direct line of sight to the treatment source;

[0009] (2) lack of a treatment step that provides a polymer surface primed to receive a subsequently deposited metal oxide coating; and

[0010] (3) greater manufacturing costs associated with the purchase and maintenance of equipment required for large-scale production under vacuum conditions.

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[0011] Thus, a need exists for a polymer having a surface with a greater hydrophilicity and a method of making same.

Summary

10 [0012] In view of the foregoing and other problems, disadvantages, and drawbacks of polymers with hydrophobic surfaces, the present invention has been devised. The invention includes: (1) a polymer having a functionalized surface of greater hydrophilicity than an as-received, nonfunctionalized polymer surface; and (2) a method of making the same. The method for obtaining the functionalized surface with chemical
15 functional groups attached thereto and with greater hydrophilicity comprises the steps of providing a polymer having a nonfunctionalized surface and exposing the nonfunctionalized surface to a plasma and a reactive gas. The polymer material having a surface with increased hydrophilicity comprises a functionalized surface with a modified water contact angle less than the contact angle characteristic of an as-received,
20 nonfunctionalized polymer surface.

[0013] One object of the present invention is to provide a modified polymer packing material with increased hydrophilicity compared to an unmodified column packing material. The modified polymer packing material comprises a plurality of surfaces that

have been functionalized by exposure to a plasma and a reactive gas. The functionalized, polymer packing material has greater column efficiency compared with typical, nonfunctionalized polymer packing material.

[0014] Another object of the present invention is to provide a method of increasing
5 the hydrophilicity of a polymer surface, especially polyethylene, polypropylene, and their derivatives, comprising the steps of providing a polymer having a non-functionalized surface, exposing the non-functionalized surface to a plasma and a reactive gas, and obtaining a functionalized polymer surface.

[0015] Yet another object of the present invention is to provide a method of
10 increasing the surface hydrophilicity of conventional contact lenses, biological implants, and other polymers having non-planar structures and complex, three-dimensional shapes.

[0016] The subject matter of the present invention is particularly pointed out and distinctly claimed herein. However, both the organization and method of operation,
together with further advantages and objects thereof, may best be understood by
15 reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

Description of the Drawings

[0017] Fig. 1 is an illustration showing an isometric view of the complex, three-
20 dimensional polymer packing material.

[0018] Fig. 2 is a schematic diagram of a scrubbing column.

[0019] Fig. 3a is a graph plotting the number of transfer units (NTUs) versus the water flow rate for columns filled with functionalized or as-received polymer packing materials.

[0020] Fig. 3b is a graph plotting the NTUs versus water flow rate for columns filled
5 with functionalized or as-received polymer packing materials.

Detailed Description

[0021] A polymer having a non-functionalized surface can be enhanced by exposure to a plasma and a reactive gas to produce a functionalized surface with increased
10 hydrophilicity. The shape of the polymers may range from simple and non-planar structures, as in contact lenses, to complex, three-dimensional, or wire structures, as in polymer separation-column packing materials. **Figure 1** shows an example of a packing-material geometry with a plurality of surfaces that may be treated by the instant invention.

15 [0022] Polymers that may benefit from the instant invention include polycarbonate, polystyrene, acrylic polymers, polypropylene, polyethylene, and halogenated polymers, including the halogenated analogues of polypropylene and polyethylene. Some examples of halogenated polymers include poly-n-fluoroethylene (e.g., Teflon), poly-n-fluoropropylene, polyvinylidenedifluoride (e.g., Kynar), polyvinylchloride, and
20 combinations thereof, wherein n is an integer selected from the group of mono, di, tri, and tetra.

[0023] In one embodiment, exposure of the polymer surface to the plasma and the reactive gas can be substantially simultaneous, in which the plasma and reactive gas are

concurrently present with the polymer. In another embodiment, the exposure can be sequential, in which the plasma exposure precedes the reactive gas exposure. In one version of the invention, the exposures occur in the chamber of a plasma unit modified to incorporate an inlet for the reactive gas. The inlet may be separate from, or connected to, the plasma inlet and may comprise a valve and tube connecting the reactive gas to the plasma chamber. The reactive gas functionalizes the polymer surface by attaching chemical functional groups thereon. The plasma enhances the reactivity of the polymer surface to the reactive gas (or liquid) such that the combination ultimately results in increased surface hydrophilicity.

[0024] The plasma is at least partially comprised of a gas selected from the group of gases consisting of oxygen, nitrogen, nitrous oxide, air, the noble gases, and combinations thereof. Preferably, the plasma would contain oxygen. The reactive gas is at least partially comprised of a gas selected from the group consisting of oxides, halides, hydrazines, arsine, and combinations thereof. Examples of oxide gases include SO_x , CO_x , NO_x , ClO_2 , BrO_2 , IO_2 , and HClO_2 . Preferably, the reactive gas is SO_3 or fuming sulfuric acid vapors. Examples of halide gases include Cl_2 , Br_2 , and I_2 .

[0025] In one version of the invention, the chemical functional group may be an acidic functional group including, but not limited to a sulfonate, a phosphate, a carboxylate, or combinations thereof. In another version, the chemical functional group may be a basic functional group including, but not limited to an amine, a hydroxyl, or combinations thereof. In yet another version, the chemical functional group may be a neutral functional group including, but not limited to an alcohol, a thiol, or combinations

thereof. As described earlier, exposing the polymer surface to the plasma and the reactive gas results in a functionalized polymer surface.

[0026] One of ordinary skill in the art will appreciate that the functionalized surface may be washed with water or an alternative solvent to remove any reactive gas residue.

5 The solvent should be selected based upon the solubility of the given residue.

[0027] The functionalized polymer surface may be immersed in a liquid-phase reactant, which can be heated, to induce the growth of a metal oxide layer. Preferably, the liquid-phase reactant comprises metal alkyls, metalorganics, metal oxide solutions, and combinations thereof. The metal oxide layer is preferably comprised of an iron oxide
10 and is beneficial for further increasing the surface wettability and enhancing the mechanical and chemical durability. Following metal oxide growth, the surface may further be treated with a NaOH solution and then rinsed. The NaOH treatment improves the wettability by presumably rehydrating the metal oxide surface.

[0028] Hereafter, the present invention is described in more detail by referring to the
15 Examples.

Example 1

[0029] **Figure 1** illustrates a polymer geometry that may be treated using the instant invention. **Figure 1** also serves as a specific, but non-limiting, example of a polymer
20 packing. In this example, an experiment was conducted according to the present invention to demonstrate surface modification of two-inch polypropylene packing material, wherein the packing material is first treated with an air plasma in a small commercial plasma unit. The plasma-treated packing material was then exposed under

vacuum to sulfur trioxide vapors given off by heated fuming sulfuric acid. The polypropylene packing material was then placed in a solution containing 3 millimolar $\text{Fe}(\text{NO}_3)_3$ and 11 millimolar nitric acid (approximately pH 2) and heated to 70 °C until a dark, rust-brown film formed on the polypropylene surfaces, indicating successful iron oxide deposition.

Example 2

[0030] A control experiment was conducted to characterize the hydrophilicity of a polymer surface under conditions of: (1) as-received, (2) oxygen plasma treated, and (3) SO_3 -gas sulfonated. The experimental results from the control experiment were compared to the hydrophilicity of a polymer surface under conditions of the present invention of: (4) plasma sulfonated (plasma treatment followed by sulfonation), and (5) plasma sulfonated followed by iron oxide overlayer growth. The conditions under which the experiments were conducted are summarized:

(1) As-received

[0031] Small coupons of polypropylene (PP) and polyvinylidene difluoride (PVDF) were rinsed in methanol to remove surface residue and then air dried. The contact angles were measured using a Rame – Hart contact angle goniometer and the average of three measurements was calculated.

(2) Oxygen plasma treated

[0032] Samples prepared as in (1) were then treated in an oxygen-containing (air) plasma using a low-power, laboratory-scale, cleaning plasma for approximately 10 minutes.

(3) Gas-phase sulfonated

[0033] Samples prepared as in (1) were additionally treated for 10-20 minutes in the SO_3 vapors rising from liquid SO_3 .

(4) Oxygen plasma followed by SO_3 gas sulfonation

5 [0034] Samples prepared as in (1) were further treated in an oxygen-containing (air) plasma using a low-power, laboratory-scale, cleaning plasma for approximately 10 minutes. The samples were removed and then placed in a closed container along with several milliliters of fresh fuming sulfuric acid. The samples were then exposed to the SO_3 fumes rising from the liquid for 10 minutes, but were not allowed to directly contact
10 the liquid. Finally, the samples were rinsed in clean water and blown dry.

(5) Concurrent oxygen and SO_3 gas plasma

[0035] Samples prepared as in (1) were further treated by a combined gas of air and SO_3 vapor. The SO_3 was introduced to the plasma chamber through a glass valve connected to a container of liquid SO_3 . The plasma was ignited for 15 minutes.

15 [0036] The contact angle for FeOOH films prepared on silicon wafers was measured as an additional control experiment. The initial contact angle for the film was approximately 100° . This value was much higher than expected and was considered to be caused by dehydration of the FeOOH surface. After brief treatment with 0.5 M NaOH , which rehydrated the surface, and subsequent rinsing, the water contact angle was
20 reduced to an average value of 23° . The iron oxide films were sufficiently thick that the influence of the substrate material on the contact angle was negligible. The results are summarized in Table 1.

Table 1. Summary of the contact angles measured for coupons of polypropylene (PP) and polyvinylidene difluoride (PVDF) after various surface modification. Contact angle results for the FeOOH film on Si are also included.

| Surface Treatment | Polymer | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Average |
|--|---------|---------|---------|---------|---------|---------|
| As-received | PP | 96° | 98° | 94° | -- | 96° |
| | PVDF | 84° | 86° | 86° | -- | 85° |
| O ₂ plasma only | PP | 52° | 42° | 48° | -- | 47° |
| | PVDF | 51° | 41° | 62° | 55° | 52° |
| SO ₃ gas only | PP | -- | -- | -- | -- | -- |
| | PVDF | 61° | 60° | 63° | 66° | 63° |
| O ₂ plasma then SO ₃ | PP | 0° | 0° | 0° | 0° | 0° |
| | PVDF | 42° | 43° | 41° | 42° | 42° |
| Air and SO ₃ plasma | PP | -- | -- | -- | -- | -- |
| | PVDF | 44° | 48° | 49° | 55° | 49° |
| FeOOH on silicon wafer | n/a | n/a | n/a | n/a | n/a | 23° |

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Example 3

[0037] Another experiment compared column operation when using as-received polypropylene packings to column operation when using the surface-functionalized packing material described in Example 1. Referring to **Figure 2**, a simple column **21** was constructed from plexiglass that had an active area of 1 ft. x 1 ft. and a height of 5 ft. The column was filled **22** with either the surface-functionalized packing material from Example 1 or the as-received polypropylene material. Air was blown into the bottom of the column using an electric fan **23**. Ammonia (NH₃) **24**, was added to the air stream, flowed through the column **21**, and exhausted into a laboratory hood. Water **25** was

sprayed over the top of the column and allowed to percolate through the packing material
22 and out of the column. Although the experimental configuration would not allow the
air flow rate to be varied, the ammonia inlet concentration and the water flow rate were
varied. The ammonia concentration was measured at the inlet and outlet streams by
5 drawing an aliquot of air through a tube containing an indicator sensitive to ammonia
concentration.

[0038] The experimental results are expressed in terms of the *number of transfer
units* (NTUs). The NTU value can be used to quantitatively compare the as-received and
surface-functionalized packing materials. The NTU value can also be used to calculate
10 the efficiency of a particular column design. In general, for a given column area and set
of operating conditions, the height necessary to achieve a desired analyte concentration in
the output stream is inversely proportional to the number of NTUs.

[0039] The NTU for the laboratory-scale column was determined for a variety of
water flow rates and input ammonia concentrations. **Figures 3a** and **3b** show results for
15 ammonia flow rates of 1.2 standard cubic feet per minute (SCFM) and 0.4 SCFM,
respectively. The data points are fitted with a second order polynomial line to emphasize
the general trend. For both the surface-functionalized and as-received polymer packing
material, the efficiency of the column increased with increasing water flow rates up to a
maximum value. The NTUs did not strongly depend on the flow of ammonia gas,
20 suggesting that considerably higher flow rates of ammonia could be tolerated before the
efficiency would be negatively affected.

[0040] Most significantly, the NTUs were substantially greater for the surface-
functionalized polymer packing material than for the as-received packing material. At

the lowest water flow rates, the functionalized packing material is almost twice as efficient as the as-received packing. The improved performance of the functionalized packing is attributed to the enhanced wettability of the surface, which is a direct result of the surface functionalization of the present invention.

- 5 **[0041]** While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims, therefore, are intended to cover all such changes and modifications as they fall within the true spirit and scope of the invention.